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OFFICE OF RESEARCH ADMINISTRATION

RESEARCH PROJECT INITIATION

Date: April 17, 1972

Project Title: Research Initiation – Preferential Metal Deposition on Tungsten in Tungsten Zirconia Composites

Project No: E-18-605

Principal Investigator: Dr. J. K. Cochran, Jr.

Sponsor: National Science Foundation

Agreement Period: From April 1, 1972 Until March 31, 1974*

*18 month budget period plus 6 months for submission of required reports, etc.

Type Agreement: Grant No. GH-32649

Amount: $16,000 NSF funds (E-18-605)
10,003 Ga. Tech Contribution
$26,003 Total

Reports Required: Annual Letter Technical; Final Report

Sponsor Contact Person (s):

Administrative
Mr. Wilbur W. Bolton, Jr.
Grants Officer
National Science Foundation
Washington, D. C. 20550

Technical Matters
Dr. R. J. Reynik
Acting Program Director
Engineering Materials Program
Division of Materials Research
National Science Foundation
Washington, D. C. 20550

Assigned to: School of Ceramic Engineering

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SPONSORED PROJECT TERMINATION

Date: 11/22/77

Project Title: "Research Initiation - Preferential Metal Disposition on Tungsten in Tungsten Zirconia Composites."

Project No: E-18-605

Project Director: Dr. J. K. Cochran, Jr.

Sponsor: National Science Foundation

Effective Termination Date: 3/31/74

Clearance of Accounting Charges: 3/31/74

Grant/Contract Closeout Actions Remaining: NONE

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GEORGIA INSTITUTE OF TECHNOLOGY
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SCHOOL OF
CERAMIC ENGINEERING

October 23, 1974

Dr. R. J. Reynik
Program Director
Engineering Materials Program
Division of Materials Research
National Science Foundation
Washington, D. C. 20550

Dear Dr. Reynik:

Attached is the annual progress report for the research initiation grant "Preferential Metal Deposition of Tungsten in Tungsten-Zirconia Composites", NSF Grant No. GH-32649 and Georgia Institute of Technology Contract No. E-18-605. This report covers the period 4-1-72 to 3-31-73.

In summary, preferential deposites of copper and cobalt on the metal portion of ZrO_2-W, UO_2-W, and Gd_2O_3-Mo unidirectional composites have been accomplished using electrochemical deposition. Desired control of deposit morphology and uniformity has not been achieved due primarily to variation of the composite fiber electrical resistance. Some improvements in deposit uniformity have been shown by applying thin films of semiconductor on the composites to act as series resistors and equilize composite fiber resistance.

Ion milling of the oxide-metal composite is being investigated as a method of preferentially removing the oxide matrix and leaving exposed fibers. While this does not fall under the category of metal deposition, it would accomplish the primary goal of producing exposed metal fibers above the oxide matrix. For use as electron emitters, this is preferred to metal deposition since the fibers exposed by ion milling would be single crystal tungsten or molybdenum.

For further details, please refer to the attached report.

Sincerely yours,

Joe K. Cochran, Jr.
Assistant Professor
School of Ceramic Engineering

JKC:lac
Attachment

Report No. E-18-605-1

PREFERENTIAL METAL DEPOSITION ON TUNGSTEN IN TUNGSTEN ZIRCONIA COMPOSITES

Annual Technical Report

(Period 4-1-72 to 3-31-73)

Project Director: Joe K. Cochran

NSF Grant No. GH-32649

School of Ceramic Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

Preferential Metal Deposition on Tungsten in Tungsten-Zirconia Composites

I. Introduction

Composites of continuous, parallel metal fibers in oxide matrices have exhibited outstanding promise as field effect electron emittors. Produced by unidirectional solidification, these composites contain continuous parallel fibers 0.1 to 1.0 microns in diameter with fiber densities from 30 to 50 million fibers/cm^2.

In the last three years, much progress has been made in the electron emission performance of these composites[1, 2, 3, 4]. Several emitter samples have produced currents of 0.5 amperes/cm^2. One sample has emitted at the 3 milliamp/cm^2 level for over 1000 hours with no damage to the sample. Of equal significance is the recent reduction of current noise to the one percent level by in situ high temperature processing of the composite[5].

Most of the emission samples tested at Georgia Tech have been a composite with an uranium oxide matrix and tungsten fibers (UO_2-W). The two major reasons for concentration on UO_2 - W is that (a) the most controllable and consistant geometries have been obtained with this system and (b) chemical etches were developed that allowed removal of the oxide to expose the tungsten fibers above the surface and other etches allowed pointing the fiber tips into conical geometries.

Emission parameters that have been investigated are effect of fiber height above the oxide matrix, geometry of the fiber tip, electric field strength, and interelectrode spacing. Theorectical analysis predicted electric field enhancement as fiber height above the matrix increased and experiments confirmed this[6]. Best experimental results were achieved with fibers extending from 5 to 35 μm from the oxide matrix.

At the start of this program, the only two oxide-metal systems that could be unidirectionaly solidified to produce usable geometries for field emission were UO_2-W and Y_2O_3- stabilized -ZrO_2 with tungsten fibers (ZrO_2-W). No successful chemical etches were developed for the ZrO_2-W composites and emission testing of ZrO_2-W was not pursued. In the last two years, a number of other oxide metal composite systems have been developed with structures suitable for field emission but methods for extending the fibers above the oxide matrix have not been found. A list of available oxide-metal composites is presented in Table 1[6]. Other than UO_2-W, the only other system that has shown partial success in exposing the fibers using selective chemical etching has been CeO_2 doped Gd_2O_3-Mo.

With the number of usable systems increasing, it would be desirable to develop a method of extending the metal conductor above the oxide matrix that would be applicable to all systems. The major material requirement for the metallic extension is high temperature capability since it is necessary to heat the emission tips to 1100°C in vacuum for removal of oxide monolayers.

This investigation has been directed toward developing a method of extending the conductor by preferential metal deposition on the metallic portion of the composites. In the original proposal, the composite system to be investigated was ZrO_2-W but with the development of additional composite systems the investigation was broadened to include them. Also, preferential metal deposition by vapor deposition was the only technique originally proposed but both electrochemical deposition and ion beam milling of the composite surface were included since both techniques would be applicable to all the systems in Table 1. Thus this report will discuss the three deposition techniques investigated: (a) Preferential Vapor Deposition, (b) Preferential Electrochemical Deposition, and (c) Preferential Ion Milling.

TABLE 1. Oxide Matrix - Metal Fiber Systems Forming Ordered Composite Geometries

1. UO_2-W	6. CeO_2 doped Gd_2O_3-W
2. Y_2O_3 Stabilized ZrO_2-W	7. CeO_2 doped Nd_2O_3-Mo
3. Y_2O_3 Stabilized HfO_2-W	8. CeO_2-Mo
4. UO_2-Ta	9. CeO_2 doped Y_2O_3-Mo
5. CeO_2 doped Gd_2O_3-Mo	10. CeO_2 doped Y_2O_3-W

II. Preferential Metal Deposition

At the start of this program, it was necessary to evaluate the engineering parameters necessary not only to produce a preferential metallic deposit on the tungsten fibers but also to meet the requirements of practical processing and stable electron field emission. In order to meet the requirements of preferential vapor deposition on the metallic portion of the oxide-metal composite, the following should exist:

1. A metallic vapor beam density lower than the critical flux necessary to cause condensation on the oxide and higher than the critical condensation flux for tungsten.

2. Condensation of the metallic film on the tungsten fibers must not promote metallic deposits on the oxide portion of the composite.

The second requirement is of primary importance considering there are 10^7 fibers/cm^2 inthe oxide-metal composites.

Lower limits of vapor beam densities had to be set, since as mentioned earlier, the preferential deposits had to extend on the order of five micrometers above the oxide surface for electron emission performance. Techniques are available for producing vapor beam densities from 10^{11} to 10^{17} atoms/cm^2 sec. or deposition rates of approximately 10^{-4} to 10^2 Å/sec. To deposit a film 5 um thick at 10^{14} atom/cm^2 sec. would require approximately 50 hours and from a practical viewpoint this had to be selected as the lowest usable beam density.

In order to achieve stable emission, it is necessary that the emitter be heated to 800 to 1000°C in a high vacuum (10^{-8} torr) to remove absorbed oxide layers. This severely limits the choice of many metals for which critical condensation effects have been measured. In fact, since the start of this contract, it has been shown that even gold with a vapor pressure of 10^{-3} torr at 1210°C is not suitable as a fiber extendor based on emission results.[6] This was demonstrated when gold was vapor deposited on conical shaped W pins extending from the UO_2 surface. After emission testing at moderate current levels, scanning electron micrographs showed that the gold had been removed from the tungsten pins. Thus, the choice of the metal for extending the pins becomes limited to materials with vapor pressures less than 10^{-3} torr at 1210°C and probably is more restrictive than this. The possible metals meeting this requirement are shown in Table II. Metals more refractory than those in Table II have too small an evaporation rate to be conventionally vapor deposited and electron gun evaporation is preferred. Thus, they were excluded from consideration for preferential metal deposition in this section.

To assess the vapor flux necessary for critical condensation a survey was made of literature values. In one of the more complete studies, Bennett, etal[7], reported critical condensation for cadmium, zinc, lead, silver, indium, antimony and bismuth on glass substrates heated to temperatures between 20 and 400°C. They reported no critical condensation effects for aluminum, tin,

TABLE II

Metals Meeting High Temperature Requirements of Electron Emission And Conventional Vapor Deposition

Metal	Vapor Pressure at 1225°C (Torr)	Temperature at Which Vapor Pressure is 10^{-3} Torr
Cr	6×10^{-4}	1280
Ge	6×10^{-4}	1280
Fe	1×10^{-4}	1330
Ni	7×10^{-5}	1380
Pd	5×10^{-5}	1380
Co	5×10^{5}	1380
Si	3×10^{-5}	1430
La	6×10^{-6}	1530
Ti	1×10^{-6}	1580
V	6×10^{-8}	1680
Rd	10^{-8}	1880
Pt	10^{-8}	1930
B	10^{-8}	1930

copper, gold, and chrominum on the glass substrates even at substrate temperatures as high as 400°C and vapor flux densities as low as 10^{12} atoms/cm^2sec. Unfortunately, they did not present sufficient data to calculate critical vapor flux as a function of substrate temperature except for antimony, Table III. It was discouraging that even for a metal such as antimony with an evaporation temperature of 480°C, a critical flux of 10^{14} atoms/cm^2sec. was not achieved until a substrate temperature of above 200°C was reached. Increasing substrate temperatures much above 200°C would result in re-evaporation of the film once vapor deposition was terminated.

In two other measurements of critical condensation[8,9], TableIII, the deposition rates required were too low to even be considered. Critical condensation was reported for aluminum[10,11] which had not been observed by Bennett[7]. However, electrical conduction was used as an indicator of a deposit, and this cannot be considered valid since deposits of as much as 40 to 50 Å in thickness can show no conduction due to isolated groups of atoms or channeling between deposits.

After considering the engineering restrictions imposed on producing preferential metal deposits on the metal of the oxide-metal composites, it was decided to use preferential deposition methods other than vapor deposition for the following reasons:

TABLE III. MAXIMUM BEAM DENSITY WITHOUT CONDENSATION

Reference	Metal	Substrate	Substrate Temp. (°C)	Beam Density (Atom/cm^{2}sec)	Deposition Rate (Å/sec)	Time to Deposit 5 Microns (Hr.)
7	Sb	Glass	203	10^{14}	.32	43.5
7	Sb	Glass	112	10^{13}	.032	435
7	Sb	Glass	50	10^{12}	.0032	4,350
8	Ag	Glass	192°C	$<10^{11}$	<.0026	$>10^4$ hr
9	Cd	NaCl	27	3.8×10^{13}	.15	175
9	Cd	LiF	27	4.2×10^{13}	.15	175

1. From the literature search, no refractory metals have been shown to exhibit critical condensation on oxides or any other material.

2. If critical condensation does exist on oxides for the refractory metals, it would be necessary to use unreasonably low deposition rates or extremely high substrate temperatures.

3. If preferential deposition did occur in the initial stages of deposition, there is a high probability that before the 0.3 micron diameter fibers could be extended to a useable emitter height, the fibers would provide nucleation sites for the film to spread across the oxide surface. Once this occurs, deposition would proceed at an equal rate over the surface since the sticking coefficient of a metal on itself is one.

4. With the development of oxide-metal composite systems other than UO_2-W and ZrO_2-W since the start of this program, Table I, it was desirable to develop a preferential deposition method that would not be as dependent on the type of oxide or metal phases present.

The property that has the greatest variation between the metal fibers and the oxide matrix is electrical conductivity and this is common in all the oxide-metal composites. Thus, to use this wide variation advantageously, electrochemical deposition was the first method attempted to produce preferential metal deposites on the fiber portion of the oxide-metal composites.

III. Preferential Electrochemical Deposition

Deposition of metallic ions from solution on metal substrates requires an electron transfer from the metal to the ion and consequently a current through the substrate. If unidirectional oxide-metal composites are used as an electron transfer medium parallel to the metallic fibers, the current is carried through the fibers and essentially none through the oxide matrix. Thus, electrochemical deposition on unidirectional oxide-metal composites occurs on the metal fibers when the composite is used as the cathode of an electrolysis cell.

For the deposition reported in this section, a cell was assembled as shown in Figure 1. The oxide-metal composite served as the cathode in either a $CuSO_4$ or $CoSO_4$ aqueous solution, with platinum as the

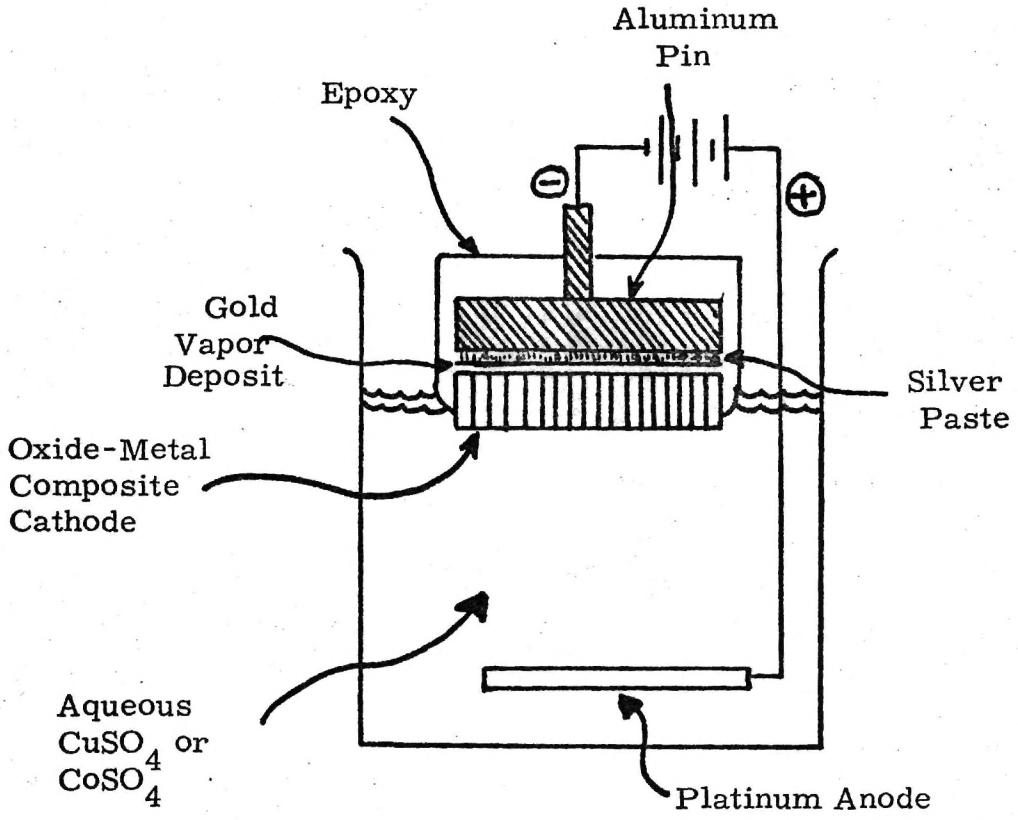


Figure 1 - Electolysis Cell for Preferential Metal Deposition on Metal Portion of Oxide-Metal Composite

anode. The cathode was prepared by slicing a rod of oxide-metal composite perpendicular to the axes of the fibers, polishing the resulting disc to a one micron diamond finish on both sides, and vapor depositing gold on one surface for electrical contact. The composite disc was silver pasted to an aluminum pin and encapsulated in epoxy to prevent electrical shorting of the aqueous solution to the aluminum pin. With this arrangement, a deposition on the cathode would require electron transfer through the pin.

Both polycrystalline and fiberous deposites were produced under a variety of electrolyte concentrations, current densities, voltages, and impurity levels. Polycrystalline and fiberous deposites will be discussed individually with only significant results being presented. Experimental details will be tabulated in the final report.

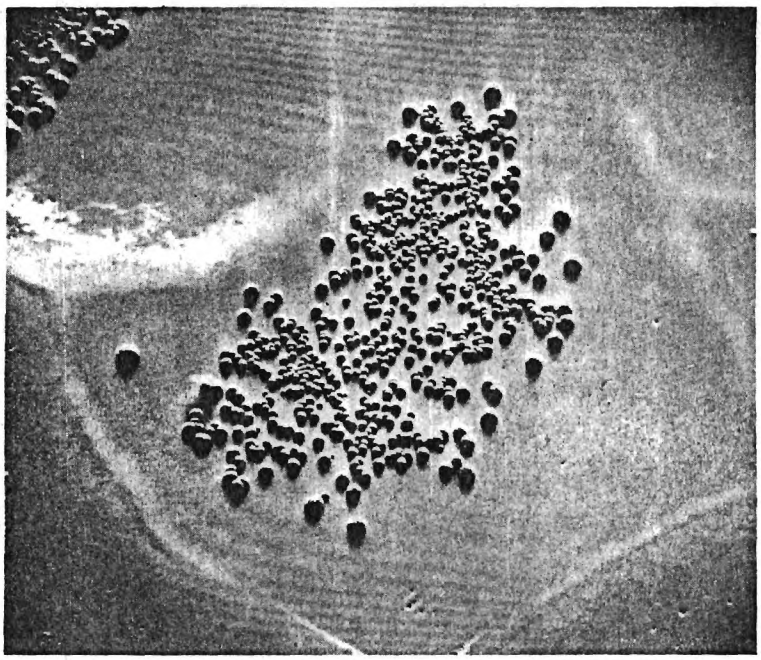
A. Polycrystalline Deposites

All the polycrystalline deposites were produced at low current levels on the order of 10^{-4} and 10^{-5} amps on samples of 0.25 cm^2. Since, the volume of the fibers in the composite is on the order of three percent, this is

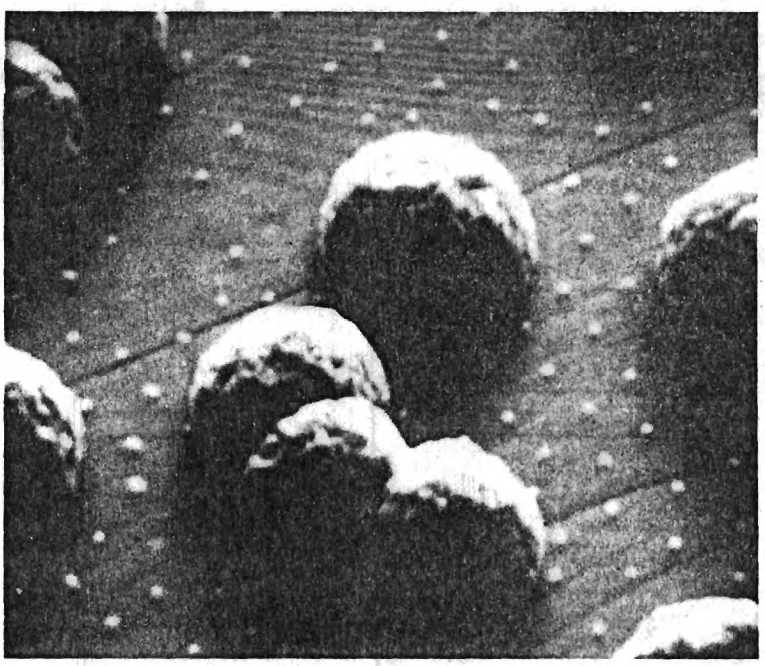
a current density of approximately 10^{-2} to 10^{-1} amps/cm^2 based on fiber portion. It was observed in initial deposites on ZrO_2-W, UO_2-W, and Gd_2O_3-Mo that the deposites were hemispherical and varied widely in size. A typical electron micrograph of the deposites is shown in Figure 2.

The size variation was thought to be caused by a variation of resistance from fiber to fiber in the composite. Certainly as can be seen in Figure 2b, a major portion of the fibers conducted no current as evidence by a lack of deposit. In addition when deposites formed on two or three adjacent fibers, the hemispheres would join and grow to single hemispherical deposites. Where deposites could be found that were associated with single fibers, variation in the deposit size indicated that there was a resistance variation from fiber to fiber since the volume of the deposit would be proportional to the current through the fiber and inversely proportional to the resistance. With the current resistance variation from fiber to fiber, there was no way of knowing the current density through a particular fiber.

There was no means of eliminating the problem of discontinuous fibers in the composite but it should be possible



a) X200.



b) X5500.

Figure 2. Scanning Electron Micrographs of Copper Electrodeposits on ZrO_2-W, Sample 18-11, Slice 13.

to equilize the resistance from fiber to fiber if a thin layer (1000 to 2000 Å)of semiconductive SiC was deposited on the composite prior to overcoating with gold. Using this technique the most uniform deposites were produced. There was still a size variation but most of the deposites could be confined to individual fibers. With an investigation of coatings of higher resistance, even more uniformity should be achievable.

Since the polycrystalline deposites had a hemispherical morphology, they could be grown only to a height of 2.5 microns before they combined with adjacent deposit. (Composite fibers are typically spaced on 2.5 micron centers.) Since this geometry was unsuitable for electron emission, attempts were made to grow single crystal whiskers or fibers as an extension of the composite fibers.

B. Fiberous Deposites

Price, et. al. [12], have reported conditions necessary for electrolytic single crystal whisker growth. In summary, the conditions necessary for such growth are (a) a critical current density ranging from 0.3 to 25 amps/cm^2, (b)

an ion concentration of one to six normal, and (c) small concentrations (0. 1 to 1 g/liter) of impurity ions such as gelatin or oleic acid. Under these conditions, single crystal whiskers of copper and silver have been grown to lengths of hundreds of microns with fiber diameters of 1 to 20 microns. The impurity gelatin or oleic acid serves to prevent growth on certain crystal faces, forcing growth into one direction.

If the metal ion concentration is too low, whisker growth is stopped becasue diffusion of ions to the growing tip is too slow to maintain the critical current densities. For the purpose of growing a high density of electrolytic whiskers on the oxide-metal composites, stirring of the solution was necessary to prevent reduction of the ion concentration below the cirtical value in the localized area of the whisker tips.

Using solutions of $CoSO_4$ with small concentrations of gelatin, whiskers of cobalt were grown almost randomly parallel to the surface of Gd_2O_3-Mo composites (i. e. perpendicular to the composite fibers.) The parallel growth was due to motion of

the solution across the composite surface due to stirring. The random growth was thought to be due again, to variation of resistance from fiber in the composite. For the reasons, presented in Section III B, use of semiconductive coating should improve uniformity of whisker growth on the oxide metal composite.

IV. Preferential Ion Beam Milling

Ion beam milling was thought to offer the potential of selectively extending fiber in the composites above the oxide matrix by selectively milling the matrix at a faster rate than the fibers. This phase is reaching completion and will be reported in detail in the final report.

In summary, six different oxide metal composite systems have been ion milled using argon, oxygen, and nitrogen ions. In addition, the samples have been subjected to both positive and negative voltages to preferentially control the milling rate of the metal and the oxide matrix. Some voltage effects have been observed but they are secondary compared to the type of ion used for milling.

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Report No. E-18-605-2

PREFERENTIAL METAL DEPOSITION ON TUNGSTEN IN TUNGSTEN ZIRCONIA COMPOSITES

Final Technical Report

(Period 4-1-72 to 9-31-73)

Project Director: Joe K. Cochran

NSF Grant No. GH-32649

School of Ceramic Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

Foreword

This research was supported by the National Science Foundation under Grant No. GH-32649. The views and conclusions contained in this document are those of the author and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the National Science Foundation or the U.S. Government.

Abstract

Oxide-metal composites have demonstrated potential application as electron field emitters when the metal fibers can be selectively extended above the oxide matrix. To date, selective chemical etching has been used to remove the oxide matrix in UO_2-W unidirectional composites leaving exposed W fibers. The purpose of this investigation was to investigate other techniques for preferentially extending the metal composite fibers in other oxide-metal unidirectional composites such as ZrO_2-W.

Preferential deposites of copper and cobalt on the metal fibers of several oxide-metal composites were produced using electrochemical deposition. Both polycrystalline hemispherical and fiberous deposites were produced. Desired control of deposit morphology was not achieved due primarily to variation of composite fiber electricl resistance.

Oxygen and nitrogen ion milling of oxide-metal composites produced no preferential etching effects and argon ion milling recessed the metal fibers below the oxide matrix producing conical depressions in the oxide surface. The geometry of the ion milled cones was dependent on the argon ion accelerating voltage.

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SECTION I

Introduction

Composites of continuous, parallel metal fibers in oxide matrices have exhibited outstanding promise as field effect electron emitters. Produced by unidirectional solidification, these composites contain continuous parallel fibers 0.1 to 1.0 microns in diameter with fiber densities from 30 to 50 million fibers/cm^2.

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Most of the emission samples tested at Georgia Tech have been a composite with an uranium oxide matrix and tungsten fibers (UO_2-W). The two major reasons for concentration on UO_2-W is that (a) the most controllable and consistent geometries have been obtained with this system and (b) chemical etches were developed that allowed removal of the

oxide to expose the tungsten fiber tips into conical geometries.

Emission parameters that have been investigated are effect of fiber height above the oxide matrix, geometry of the fiber tip, electric field strength, and interelectrode spacing. Theorectical analysis predicted electric field enhancement as fiber height above the matrix increased and experiments confirmed this[6]. Best experimental results were achieved with fibers extending from 5 to 35 μm from the oxide matrix.

At the start of this program, the only two oxide-metal systems that could be unidirectionally solidified to produce usable geometries for field emission were UO_2-W and Y_2O_3 - stabilized -ZrO_2 with tungsten fibers (ZrO_2-W). No successful chemical etches were developed for the ZrO_2-W composites and emission testing of ZrO_2-W was not pursued. In the last two years, a number of other oxide-metal composite systems have been developed with structures suitable for field emission but methods for extending the fibers above the oxide matrix have not been found. A list of available oxide-metal composites is presented in Table I[6]. Other than UO_2-W, the only other system that has shown partial success in exposing the fibers using selective chemical etching has been CeO_2 doped Gd_2O_3-Mo.

With the number of usable systems increasing, it would be desirable to develop a method of extending the metal

Table I. Oxide Matrix - Metal Fiber Systems Forming Ordered Composite Geometries.

1.	UO_2-W	6.	CeO_2 doped Gd_2O_3-W
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5.	CeO_2 doped Gd_2O_3-Mo	10.	CeO_2 doped Y_2O_3-W

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This investigation has been directed toward developing a method of extending the conductor by preferential metal deposition on the metallic portion of the composites. In the original proposal, the composite system to be investigated was ZrO_2-W but with the development of additional composite systems the investigation was broadened to include them. Also, preferential metal deposition by vapor deposition was the only technique originally proposed but both electrochemical deposition and ion beam milling of the composite surface were included since both techniques would be applicable to all the systems in Table I. Thus this report will discuss the three deposition techniques investigated; (a) Preferential Vapor Deposition, (b) Preferential Electrochemical Deposition, and (c) Preferential Ion Milling.

SECTION II

Preferential Metal Deposition

At the start of this program, it was necessary to evaluate the engineering parameters necessary not only to produce a preferential metallic deposit on the tungsten fibers but also to meet the requirements of practical processing and stable electron field emission. In order to meet the requirements of preferential vapor deposition on the metallic portion of the oxide-metal composite, the following should exist:

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Lower limits of vapor beam densities had to be set, since as mentioned earlier, the preferential deposits

had to extend on the order of five micrometers above the oxide surface for electron emission performance. Techniques are available for producing vapor beam densities from 10^{11} to 10^{17} atoms/cm^{2}sec. or deposition rates of approximately 10^{-4} to 10^{2} Å/sec. To deposit a film 5 μm thick at 10^{14} atom/cm^2 sec. would require approximately 50 hours and from a practical viewpoint this had to be selected as the lowest usuable beam density.

In order to achieve stable emission, it is necessary that the emitter be heated to 800 to 1000°C in a high vacuum (10^{-8} torr) to remove absorbed oxide layers. This severely limits the choice of many metals for which critical condensation effects have been measured. In fact, since the start of this contract, it has been shown that even gold with a vapor pressure of 10^{-3} torr at 1210°C is not suitable as a fiber extendor based on emission results [6]. This was demonstrated when gold was vapor deposited on conical shaped W pins extending from the UO_2 surface. After emission testing at moderate current levels, scanning electron micrographs showed that the gold had been removed from the tungsten pins. Thus, the choice of the metal for extending the pins becomes limited to materials with vapor pressures less than 10^{-3} torr at 1210°C and probably is more restrictive than this. The possible metals meeting this requirement are shown in Table II. Metals more refractory than those in Table

Table II. Metals Meeting High Temperature Requirements of Electron Emission and Conventional Vapor Deposition.

Metal	Vapor Pressure at 1225°C (Torr)	Temperature at Which Vapor Pressure is 10^{-3} Torr
Cr	6×10^{-4}	1280
Ge	6×10^{-4}	1280
Fe	1×10^{-4}	1330
Ni	7×10^{-5}	1380
Pd	5×10^{-5}	1380
Co	5×10^{5}	1380
Si	3×10^{-5}	1430
La	6×10^{-6}	1530
Ti	1×10^{-6}	1580
V	6×10^{-8}	1680
Rd	$< 10^{-8}$	1880
Pt	$< 10^{-8}$	1930
B	$< 10^{-8}$	1930

II have too small an evaporation rate to be conventionally vapor deposited and electron gun evaporation is preferred. Thus, they were excluded from consideration for preferential metal deposition in this section.

To assess the vapor flux necessary for critical condensation a survey was made of literature values. In one of the more complete studies, Bennett, et.al.[7], reported critical condensation for cadmium, zinc, lead, silver, indium, antimony and bismuth on glass substrates heated to temperatures between 20 and 400°C. They reported no critical condensation effects for aluminum, tin, copper, gold, and chrominum on the glass substrates even at substrate temperatures as high as 400°C and vapor flux densities as low as 10^{12} atoms/cm^2 sec. Unfortunately, they did not present sufficient data to calculate critical vapor flux as a function of substrate temperature except for antimony, Table III. It was discouraging that even for a metal such as antimony with an evaporation temperature of 480°C, a critical flux of 10^{14} atoms/cm^2 sec. was not achieved until a substrate temperature of above 200°C was reached. Increasing substrate temperatures much above 200°C would result in re-evaporation of the film once vapor deposition was terminated.

In two other measurements of critical condensation[8,9], Table III, the deposition rates required were too low

Table III. Maximum Beam Density Without Condensation.

Reference	Metal	Substrate	Substrate Temp. (°C)	Beam Density (Atom/cm^2sec)	Deposition Rate (Å/sec)	Time to Deposit 5 Microns (Hr.)
7	Sb	Glass	203	10^{14}	.32	43.5
7	Sb	Glass	112	10^{13}	.032	435
7	Sb	Glass	50	10^{12}	.0032	4,350
8	Ag	Glass	192°C	$<10^{11}$	<.0026	$>10^4$ hr
9	Cd	NaCl	27	3.8×10^{13}	.15	175
9	Cd	LiF	27	4.2×10^{13}	.15	175

to even be considered. Critical condensation was reported for aluminum[10,11] which had not been observed by Bennett[7]. However, electrical conduction was used as an indicator of a deposit, and this cannot be considered valid since deposits of as much as 40 to 50 A in thickness can show no conduction due to isolated groups of atoms or channeling between deposits.

After considering the engineering restrictions imposed on producing preferential metal deposits on the metal of the oxide-metal composites, it was decided to use preferential deposition methods other than vapor deposition for the following reasons:

1. From the literature search, no refractory metals have been shown to exhibit critical condensation on oxides or any other material.
2. If critical condensation does exist on oxides for the refractory metals, it would be necessary to use unreasonably low deposition rates or extremely high substrate temperatures.
3. If preferential deposition did occur in the initial stages of deposition, there is a high probability that before the 0.3 micron diameter fibers could be extended to a useable emitter height, the fibers would provide nucleation sites for the film to spread across the oxide surface.

Once this occurs, deposition would proceed at an equal rate over the surface since the sticking coefficient of a metal on itself is one.

4. With the development of oxide-metal composite systems other than UO_2-W and ZrO_2-W since the start of this program, Table I, it was desirable to develop a preferential deposition method that would not be as dependent on the type of oxide or metal phases present.

The property that has the greatest variation between the metal fibers and the oxide matrix is electrical conductivity and this is common in all the oxide-metal composites. Thus, to use this wide variation advantageously, electrochemical deposition was the first method attempted to produce preferential metal deposites on the fiber portion of the oxide-metal composites.

SECTION III

Preferential Electrochemical Deposition

Deposition of metallic ions from solution on metal substrates requires an electron transfer from the metal to the ion and consequently a current through the substrate. If unidirectional oxide-metal composites are used as an electron transfer medium parallel to the metallic fibers, the current is carried through the fibers and essentially none through the oxide matrix. Thus, electrochemical deposition on unidirectional oxide-metal composites occurs on the metal fibers when the composite is used as the cathode of an electrolysis cell.

For the deposition reported in this section, a cell was assembled as shown in Figure 1. The oxide-metal composite served as the cathode in either a $CuSO_4$ or $CoSO_4$ aqueous solution, with platinum as the anode. The cathode was prepared by slicing a rod of oxide-metal composite perpendicular to the axes of the fibers, polishing the resulting disc to a one micron diamond finish on both sides, and vapor depositing gold on one surface for electrical contact. The composite disc was silver pasted to an aluminum pin and encapsulated in epoxy to prevent

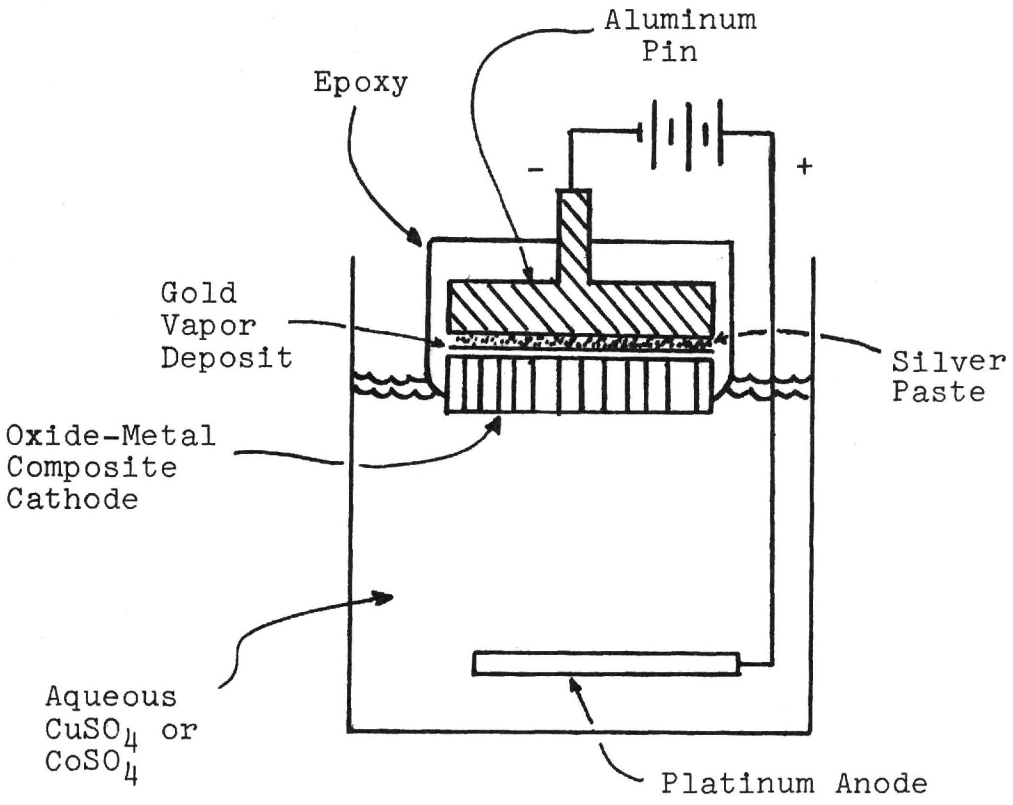


Figure 1. Electolysis Cell for Preferential Metal Deposition on Metal Portion Of Oxide-Metal Composite.

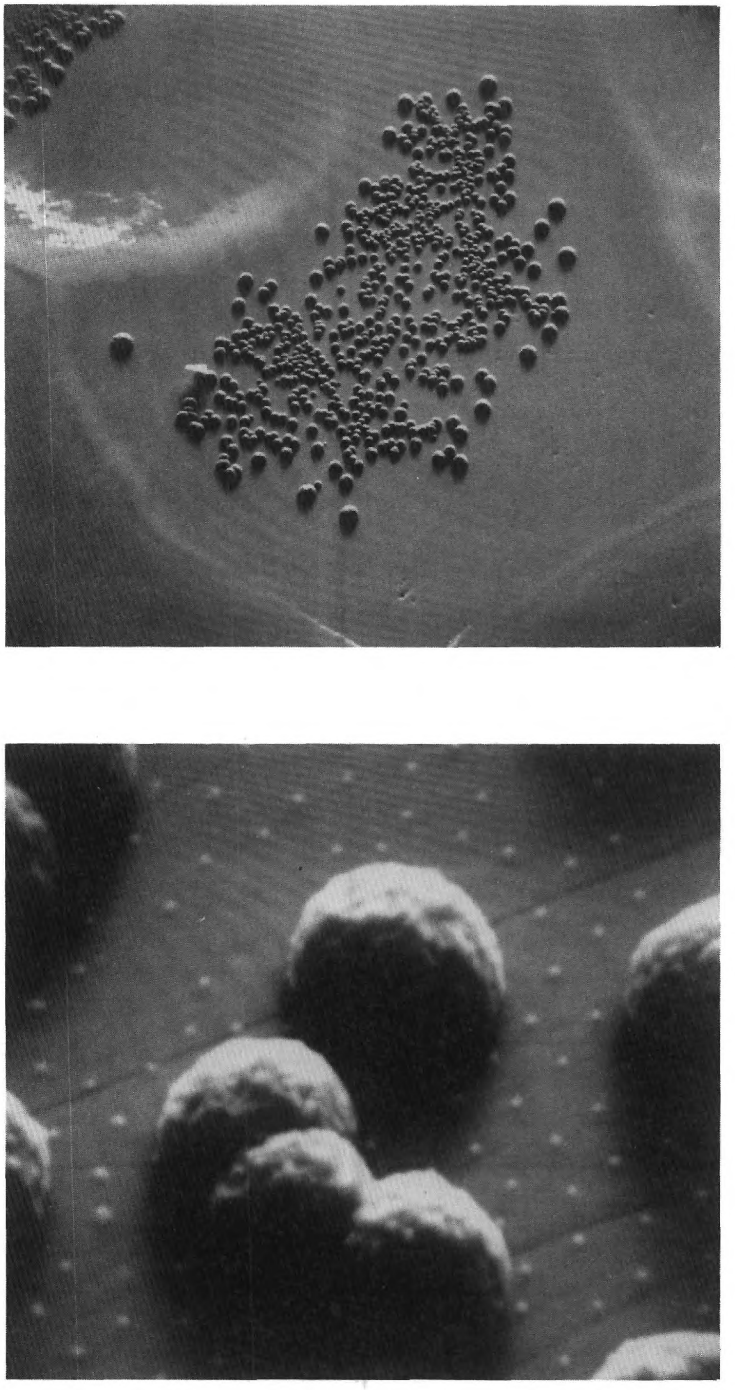
electrical shorting of the aqueous solution to the aluminum pin. With this arrangement, a deposition on the cathode would require electron transfer through the composite fibers.

Both polycrystalline and fiberous deposites were produced under a variety of electrolyte concentrations, current densities, voltages, and impurity levels. Polycrystalline and fiberous deposites will be discussed individually with only significant results being presented.

A. Polycrystalline Deposites

All the polycrystalline deposites were produced at low current levels on the order of 10^{-4} and 10^{-5} amps on samples of 0.25 cm^2. Since the volume of the fibers in the composite is on the order of three percent, this is a current density of approximately 10^{-2} to 10^{-1} amps/cm^2 based on fiber portion. It was observed in initial deposites on ZrO_2-W, UO_2-W, and Gd_2O_3-Mo that the deposites were hemispherical and varied widely in size. A typical electron micrograph of the deposites is shown in Figure 2.

The size variation was thought to be caused by a variation of resistance from fiber to fiber in the composite. Certainly as can be seen in Figure 2b, a major portion of the fibers conducted no current as evidence by a lack of deposit. In addition when deposites formed on two or three adjacent fibers, the hemispheres would join and grow to single hemispherical deposites. Where deposites



a

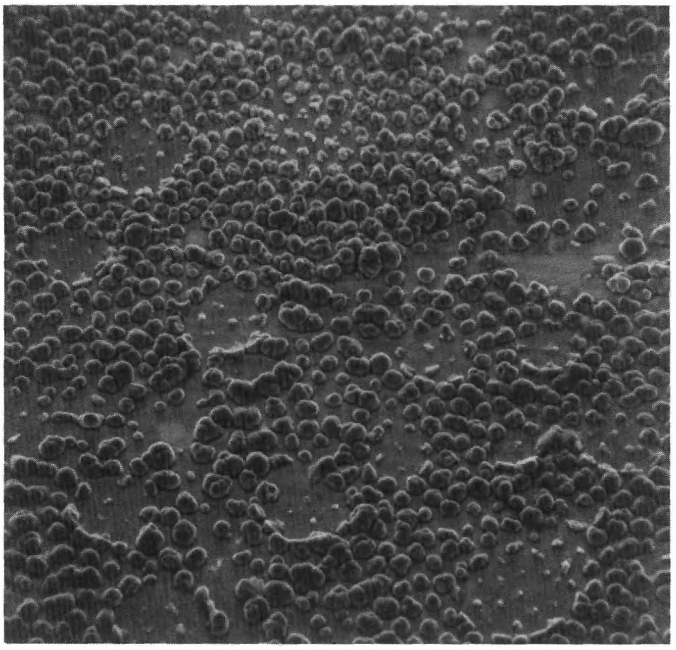
b

Figure 2. Scanning Electron Micrographs of Copper Electrodeposits on a ZrO_2-W Composite, (a) 200x and (b) 5500x, 45° Viewing Angle.

could be found that were associated with single fibers, variation in the deposit size indicated that there was a resistance variation from fiber to fiber since the volume of the deposit would be proportional to the current through the fiber and inversely porportional to the resistance. With the current resistance variation from fiber to fiber, there was no way of knowing the current density through a particular fiber.

There was no means of eliminating the problem of discontinuous fibers in the composite but it whould be possible to equalize the resistance from fiber to fiber if a thin layer (1000 to 2000 Å) of semiconductive SiC was deposited on the composite prior to overcoating with gold. Using this technique the most uniform deposites were produced. There was still a size variation but most of the deposites could be confined to individual fibers, Figure 3. With an investigation of coatings of higher resistances, even more uniformity should be acheivable.

Since the polycrystalline deposites had a hemispherical morphology, they could be grown only to a height of 1.25 microns before they combined with adjacent deposit. (Composite fibers are typically spaced on 2.5 micron centers.) Since this geometry was unsuitable for electron emission, attempts were made to grow single crystal whiskers or fibers as an extension of the composite fibers.



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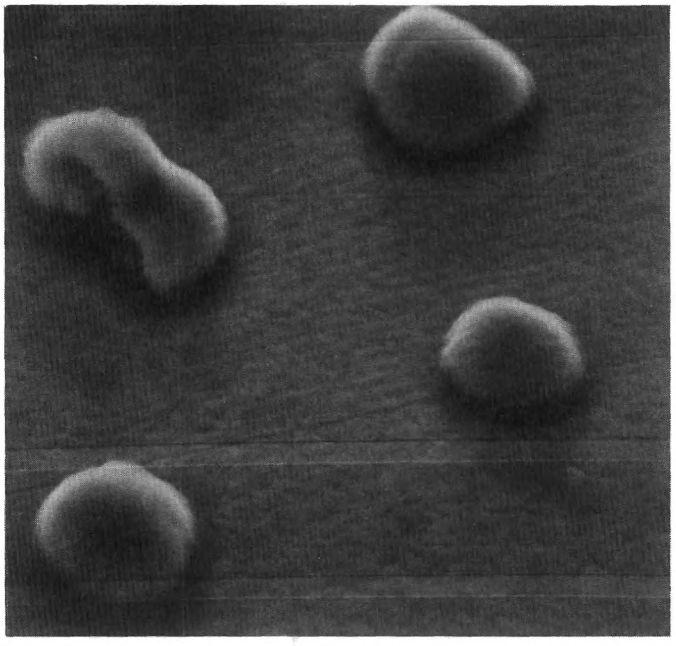


b

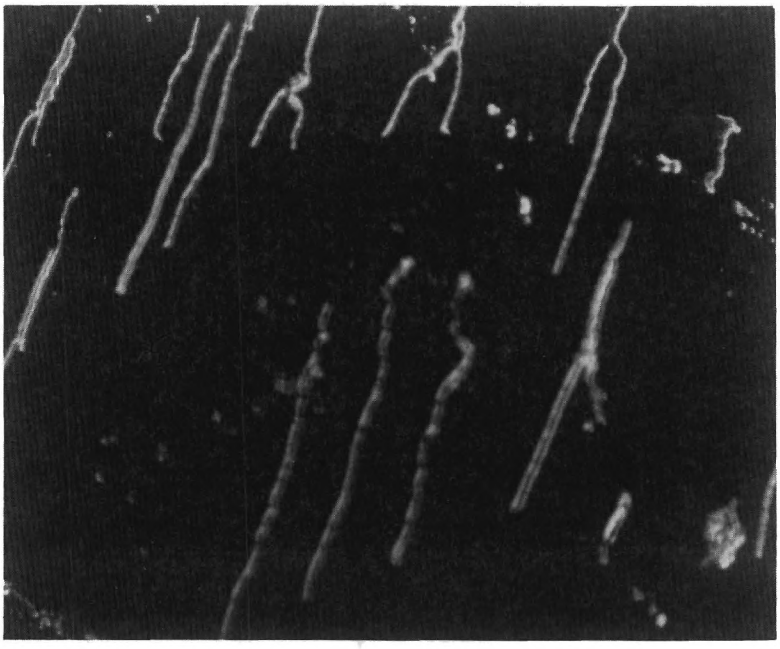
Figure 3. Scanning Electron Micrograph of Cobalt Electrodeposits on a ZrO_2-W Composite Showing Deposits Confined to Individual W Fibers, (a) 600 x and (b) 6000x, 45° Viewing Angle.

B. Fiberous Deposites

Price, et. al.[12], have reported conditions necessary for electrolytic single crystal whisker growth. In summary, the conditions necessary for such growth are (a) a critical current density ranging from 0.3 to 25 amps/cm^2, (b) an ion concentration of one to six normal, and (c) small concentrations (0.1 to 1 g/liter) of impurity ions such as gelatin or oleic acid. Under these conditions, single crystal whiskers of copper and silver have been grown to lengths of hundreds of microns with fiber diameters of 1 to 20 microns. The impurity gelatin or oleic acid serves to prevent growth on certain crystal faces, forcing growth into one direction.

If the metal ion concentration is too low, whisker growth is stopped because diffusion of ions to the growing tip is too slow to maintain the critical current densities. For the purpose of growing a high density of electrolytic whiskers on the oxide-metal composites, stirring of the solution was necessary to prevent reduction of the ion concentration below the critical value in the localized area of the whisker tips.

Using solutions of $CoSO_4$ with small concentrations of gelatin, whiskers of cobalt were grown from seemingly random W fibers with the whiskers parallel to the surface of Gd_2O_3-Mo composites (i.e. perpendicular to the composite fibers, Figure 4). The parallel growth was due to



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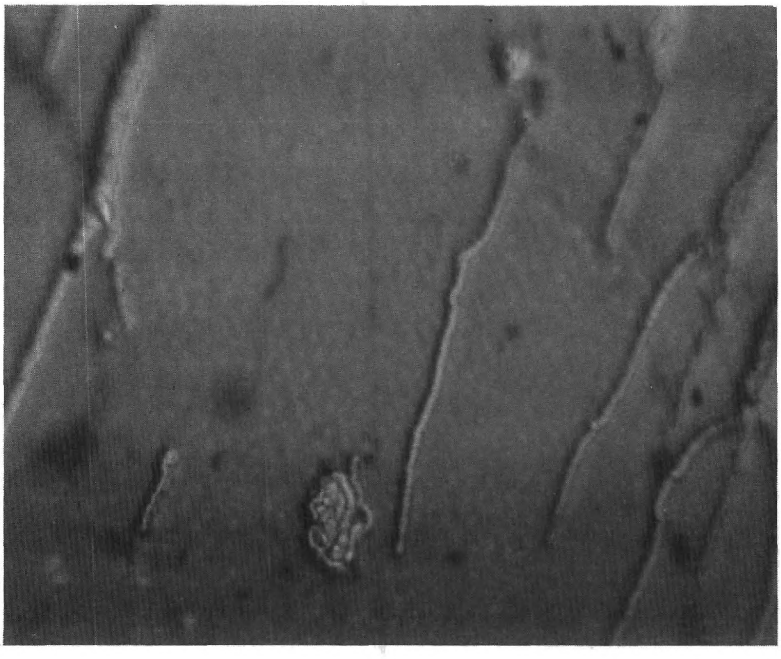


b

Figure 4. Reflected Light Micrographs of Cobalt Whiskers Electrolytically Deposited on a Gd_2O_3-W Composite, (a) 200x and (b) 600x.

motion of the solution across the composite surface due to stirring. The whisker growth at random places on the composite was thought to be due, again, to variation of resistance from fiber to fiber in the composite resulting in large variations in current density. Also on the samples with whiskers were hemispherical deposites probably resulting from current densities below the critical level need for whisker growth. The whiskers were typically 100-250 μm in length and 1-2 μm in diameter. For the reasons presented in Section III A, use of semiconductive coating should improve uniformity of whisker growth on the oxide-metal composite, but at this stage the uniformity was insufficient for field emission applications.

SECTION IV

Preferential Ion Milling

Ion milling was thought to offer the potential of selectively extending fibers in the composites above the oxide matrix by selectively milling the matrix at a faster rate than the fibers. Using a commercial ion beam gun, ion currents of up to 5 milliamperes/cm^2 at accelerating voltages of 6 to 15 KV were obtainable. All composite samples were prepared for ion milling by slicing wafers perpendicular to the fiber axes and polishing to a one micron diamond finish. The samples were ion milled perpendicular to the polished surfaces, i.e. parallel to the composite fiber axes.

Six different oxide-metal composite systems (UO_2-W, ZrO_2-W, Gd_2O_3-Mo, Gd_2O_3-W, CeO_2-Mo, and CeO_2-W) were ion milled with oxygen and nitrogen ions. The results were all similar for oxygen and nitrogen and will be summarized. The samples were typically exposed for one hour to 5 ma/cm^2 ion beams at ion accelerating voltages of 6-15 KV and the samples were held at various voltages ranging from +5 to -5 KV. Very little preferential ion milling was observed for either oxygen or nitrogen ion beams under the various

conditions. Presumable, the metal surfaces were converted to nitrides and oxides which ion milled at the same rate at the oxide matrices.

The most pronounced preferential ion milling effect was produced by argon ion bombardment of UO_2-W composites. It was discovered that argon ion milling a polished UO_2-W composite would recess the W fibers into the UO_2 matrix with the fibers centered in an inverted truncated cone, Figure 5. The ion milled cones appeared to be symmetrical with the tungsten fiber axes being the center of rotation of the cones. Thus, the cone axes were perpendicular to the matrix surface when the fibers were perpendicular to the polished surface.

One UO_2-W composite, sample Q, was noted to ion mill producing uniform cones over most of its surface and it was selected for investigation of the effect of ion energy on cone geometry. Sample Q was processed by brazing to a 0.125 inch diameter molybdenum post and polishing to a one micron diamond finish. All ion milling was carried out at an argon beam current of 5 ma/cm^2 as measured at the sample with the sample grounded for a duration of one hour. The sample was milled using ion acceleration voltages of 6.0 to 12.0 KV with the sample rotating at 60 rpm. After photographing in the SEM, the sample was repolished with one micron diamond paste to remove the previously milled surface.

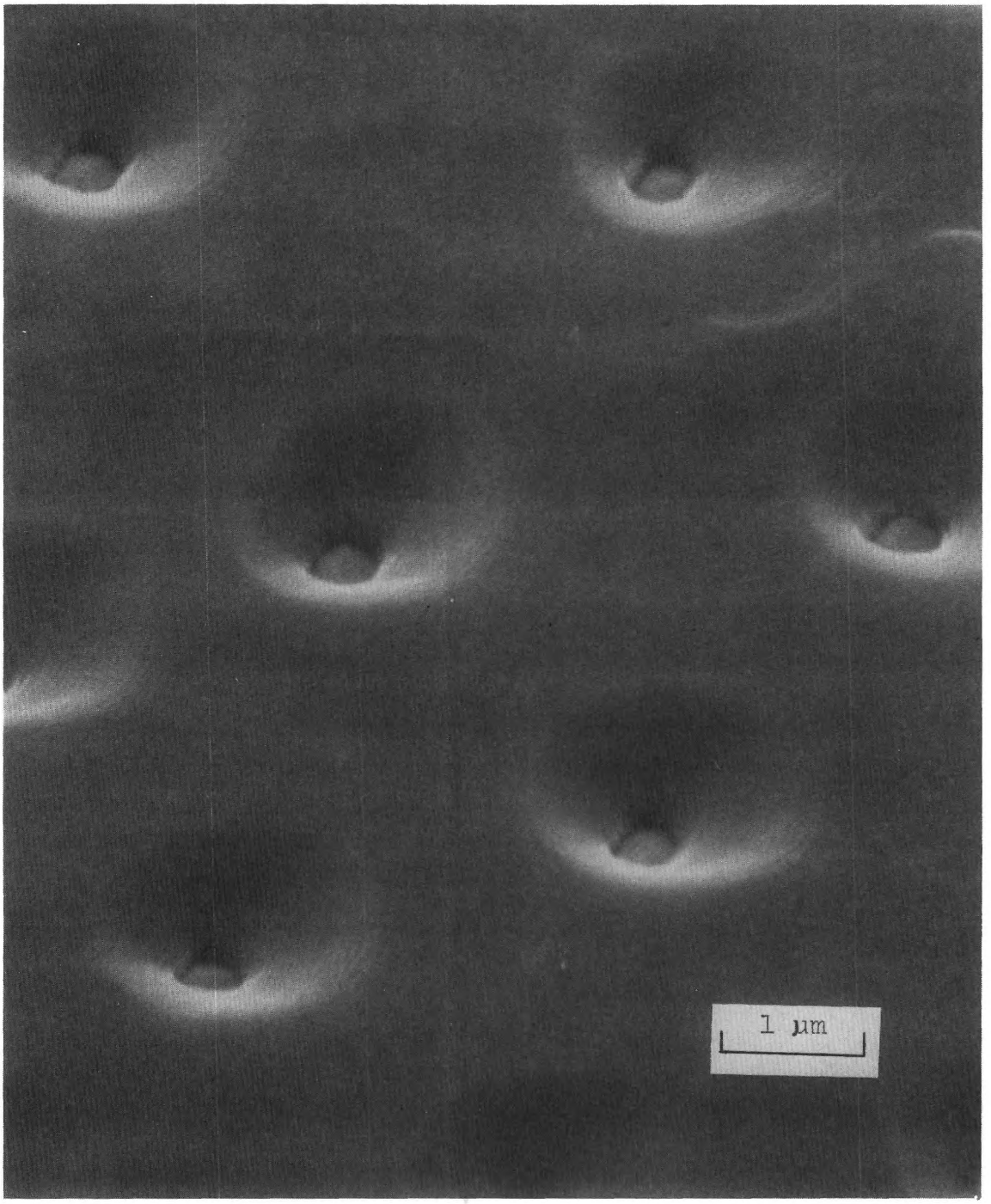


Figure 5. Scanning Electron Micrograph of an Array of Tungsten Single Crystal Fibers Recessed in Conical Depressions in a Urania Matrix. The Structure is Produced by Argon Ion Milling a Polished UO_2-W Composite With a 13 KV, 5 mA/cm^2 Beam, X22, 100, 45° Viewing Angle.

The angle of the three cones with respect to the UO_2 surface was calculated from SEM photographs for each ion energy investigated, Table IV. As can be seen in Figure 6, the cone angle with respect to the UO_2 surface increased with voltage ranging from 16° at 6 KV to 40° at 12 KV. The scatter in the data, Figure 7, is probably due largely to the cone axis not being perpendicular to the UO_2 surface and to nonsymmetrical cones as these two assumptions must be made to calculate cone angle. Using these two assumptions, the cone angle, ϕ, was calculated knowing the viewing angle in the SEM, θ, and the lengths l_1 and l_3, Figure 8.

Referring to Figure 8,

ϕ = cone angle with respect to the UO_2 surface,

θ = viewing angle in the SEM,

r = fiber radius,

d = cone depth.

and the other lengths are labeled as shown. Cone angle was calculated as follows:

$$\tan \phi = d/l_5 \tag{1}$$

$$d = l_6 \tan\theta \tag{2}$$

$$l_6 = l_7 - l_5 \tag{3}$$

Combining 1, 2, and 3,

$$\tan \phi = \frac{l_7 - l_5}{l_5} \cdot \tan\theta = \left(\frac{l_7}{l_5} - 1\right) \tan\theta \tag{4}$$

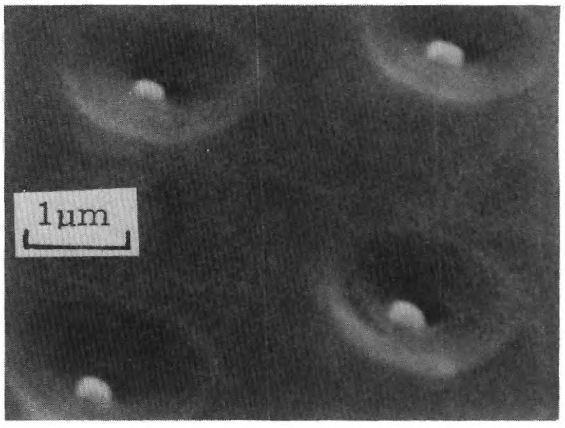
$$l_7 = l_3/\sin\theta \tag{5}$$

TABLE IV

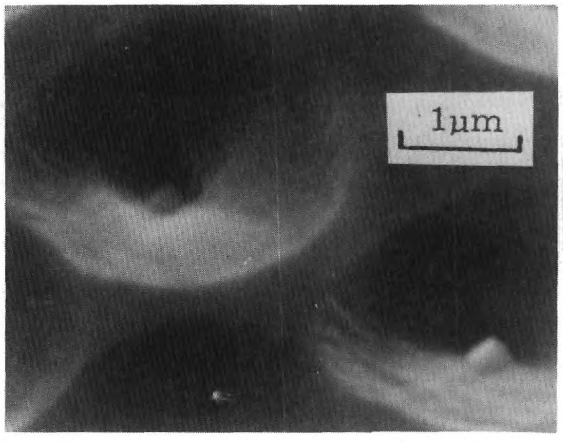
EFFECT OF ION ENERGY OF GEOMETRY OF ION MILLED CONES IN UO_2-W COMPOSITES, SAMPLE Q

Sample	Ion Energy (KV)	Cone Angle (Degrees)	Average Width of Cone at Surface (μm)	Cone Depth (μm)
25Q	6.0	16.4 ±2.8*	1.87	0.21
32Q	7.5	23.2 ±0.6*	3.00	0.59
23Q	9.0	27.9 ±1.5*	2.78	0.64
31Q	10.5	29.2 ±0.3*	3.02	0.81
28Q	12.0	39.9 ±0.5*	2.45	0.66

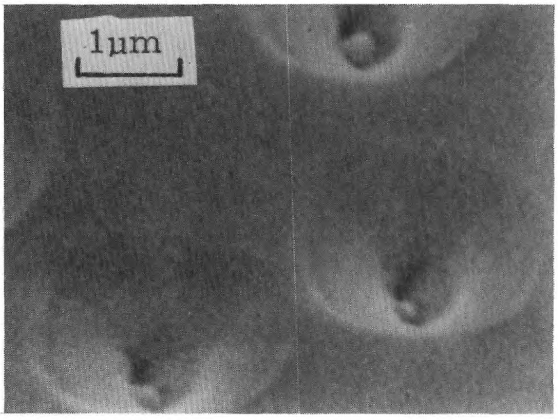
*Average of 3 cones. Error is mean deviation.



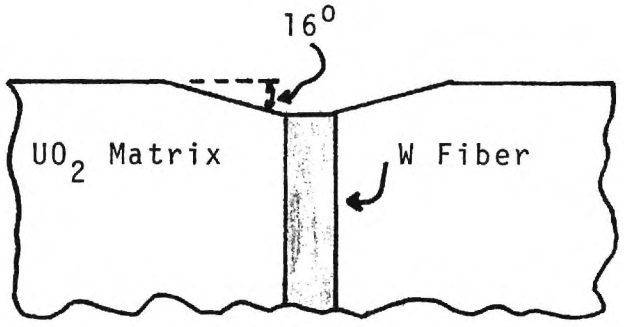
6.0 KV; 12, 100X



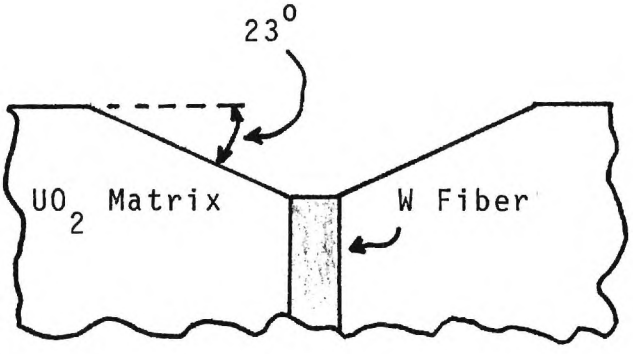
7.5 KV; 13,800X



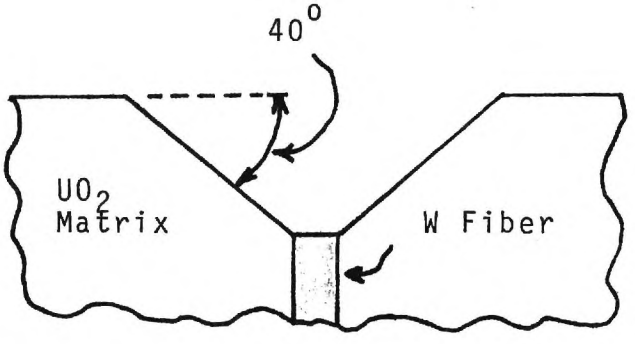
12.0 KV; 12,100X



(a) Scale 20,000X



(b) Scale 20,000X



(c) Scale 20,000X

Figure 6. Scanning Electron Micrographs of UO_2-W Composite, Sample Q, Showing Effect of Ion Energy of Angle of Ion Milled Cones. (All SEM's at Viewing Angle of 45°)

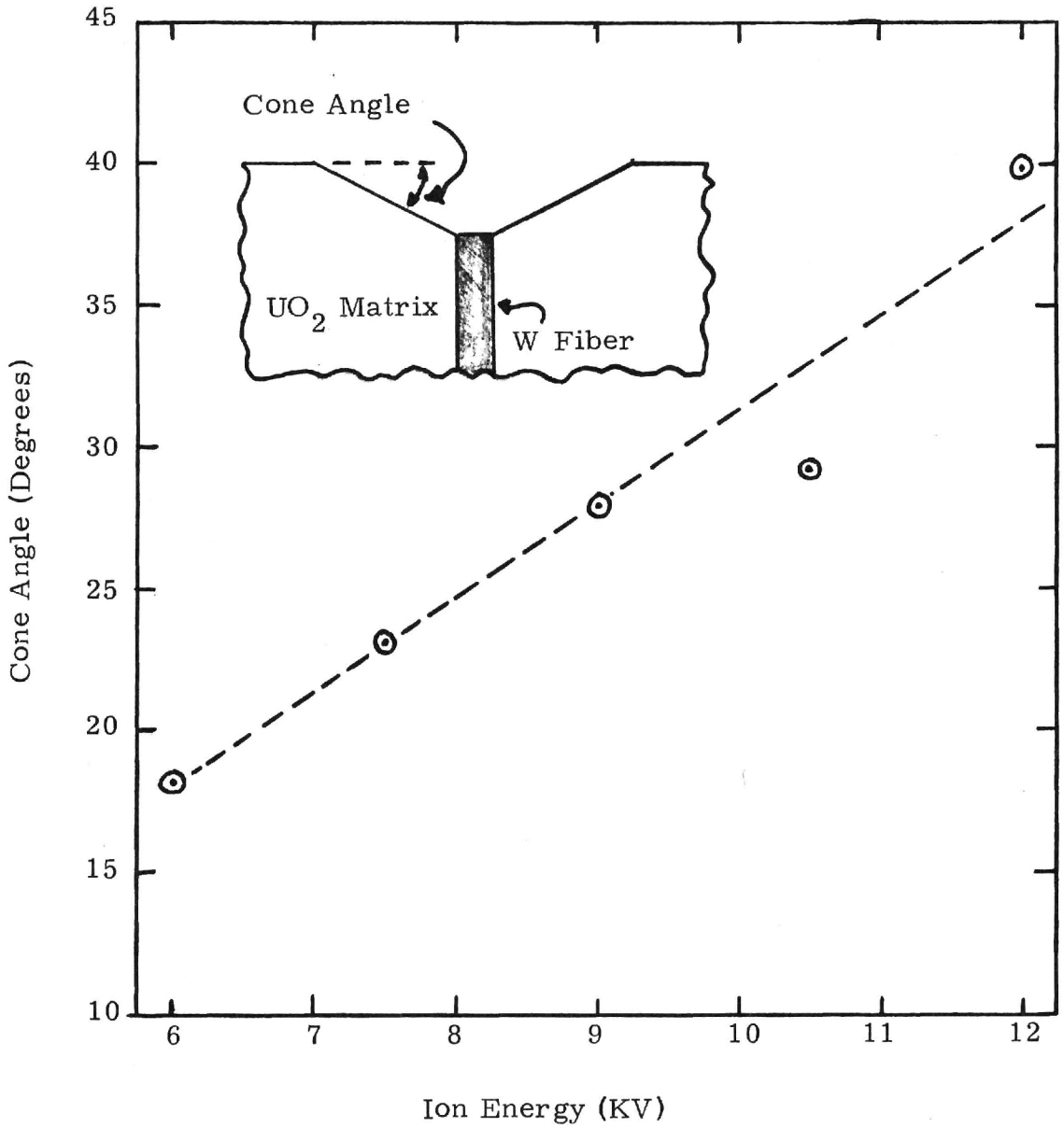
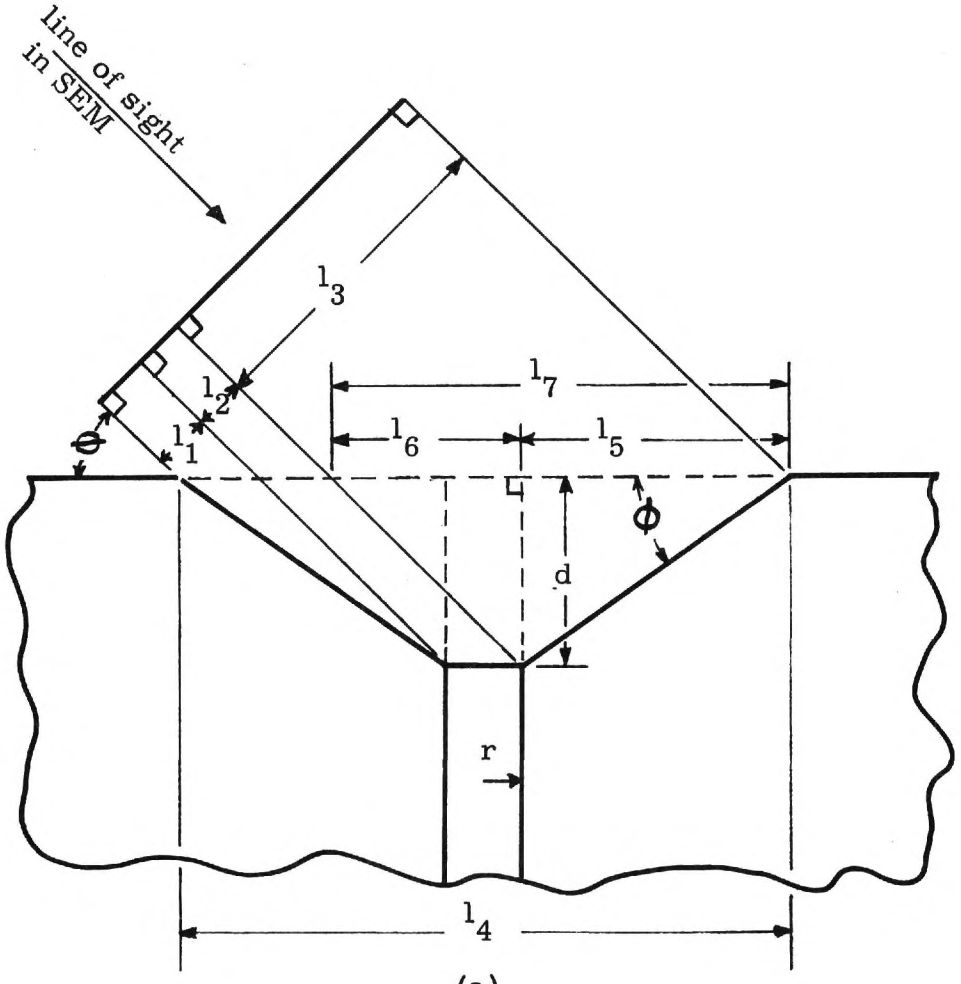
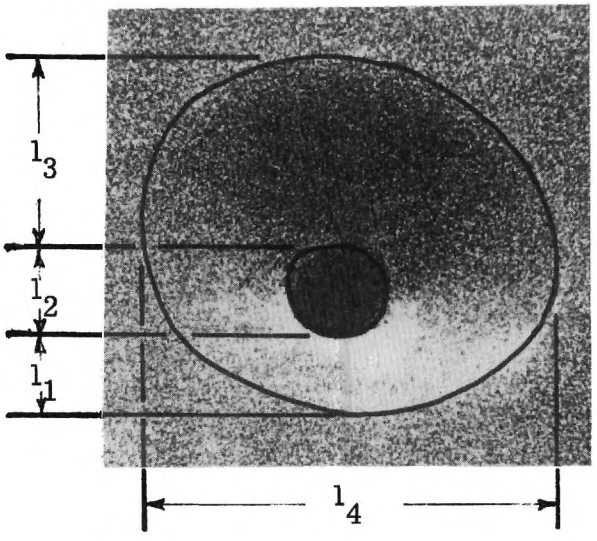


Figure 7. Effect of Ion Energy on Angle of Recessed Cones Ion Milled in UO_2-W Composite, Sample Q.



(a)



(b)

Figure 8. Parameters for Calculation of Ion Milled Cone Geometry, Shown (a) in a Side View, and (b) as Measured from a SEM Photograph

$$l_5 = \frac{l_4}{2} - r = \frac{l_4}{2} - \frac{l_2}{2\sin\theta} \tag{6}$$

$$l_4 = \frac{l_1 + l_2 + l_3}{\sin\theta} \tag{7}$$

Combining 5, 6, and 7 and rearranging,

$$\frac{l_7}{l_5} = \frac{l_3}{\sin\theta} \Big/ \frac{l_3 + l_1}{2\sin\theta} \tag{8}$$

or

$$\frac{l_7}{l_5} = \frac{2\,l_3}{l_3 + l_1} \tag{9}$$

Combining 4 and 9 and rearranging,

$$\tan\phi = \frac{l_3 - l_1}{l_3 + l_1} \cdot \tan\theta \tag{10}$$

Since for all photos $\theta = 45°$, $\tan\theta = 1$, and

$$\tan\phi = \frac{l_3 - l_1}{l_3 + l_1} \tag{11}$$

Cone depth, d, was calculated from

$$d = \frac{l_3 - l_1}{2\cos\theta} \Big/ \text{SEM Magnification} \tag{12}$$

and cone width was measured directly from the scanning electron micrographs.

At this time, the ion milled cones offer no solution to extending the metal composite fibers above the surface but the preferential ion milling effect was considered unique enough to be reported. Perhaps such a geometry will prove applicable to other uses of the composites other than field emission.

Section V

Summary

The purpose of this investigation was to develop a method of extending metal fibers in oxide-metal composites above the oxide matrix for use in electron field emitter applications. Analysis of available literature indicated that preferential vapor deposition of refractory metals on the composite metal fibers was not feasible.

Preferential deposites of copper and cobalt on the metal portion of ZrO_2-W, UO_2-W, and Gd_2O_3-Mo unidirectional composites was accomplished using electrochemical deposition. Both polycrystalling and fiberous deposites were produced. Desired control of deposit morphology and uniformity was not achieved due primarily to variation of the composite fiber electrical resistance. Improvements in deposit uniformity were produced by depositing thin films of SiC semiconductor on the reverse side of the composite to act as series resistors and equalize composite fiber resistance.

Ion milling of oxide-metal composites was investigated as a method of preferentially removing the oxide matrix to produce exposed fibers. Milling with oxygen and nitrogen

ion beams under a variety of conditions produced no preferential removal of either the metal or oxide in the composites. Argon ion milling selectively recessed the metal fibers velow the oxide matrix leaving the recessed fiber centered in inverted truncated cones in the oxide matrix. The geometry of the ion milled cones was shown to be dependent on the accelerating voltage of the ion beam.

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